

PATENT SPECIFICATION

(11) 1 520 026

1 520 026

- (21) Application No. 42126/75 (22) Filed 15 Oct. 1975
(61) Patent of Addition to No. 1 430 020 dated 19 April 1973
(31) Convention Application No. 518 002
(32) Filed 25 Oct. 1974 in
(33) United States of America (US)
(44) Complete Specification published 2 Aug. 1978
(51) INT CL³ C09D 3/50; B05D 5/00; B32B 15/08, 15/18, 15/20; C23F 7/00
(52) Index at acceptance
C3R 38C 38D3A C12 C16 C2X L1B L2X L5C L6G
B2E 191 193 197 19X 19Y 20Y 228 248 302 327 349 359 360
378 40X 40Y 410 41X 41Y 438 439 44Y 458 463 46Y
498 532 548 570 571 579 580 588 620 649 65Y 673
67Y 708 742 758 768 789 798
C7U 4E2A 4E3 4F1 4F2 4H10 4J 4M1 4M2 5 7A 7C 7G
(72) Inventors LEONARD KULICK and JOHN HOWELL



(54) PROCESSES FOR PROVIDING PROTECTIVE COATINGS ON METAL SURFACES

(71) We, PYRENE CHEMICAL SERVICES LIMITED, a British Company, of Ridgeway, Iver, Buckinghamshire, SL0 9JJ, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

Numerous techniques have been developed for protecting metal surfaces against corrosion. Of these techniques, the most common is phosphatisation of the metal surface with an aqueous solution containing phosphate ions, so as to form on the surface a corrosion resistant, non-reactive phosphate complex coating. Depending on the type of metal to be treated, the phosphate baths may be based on an alkali metal and/or ammonium phosphate or, on the other hand, may be a coating metal phosphate solution containing a coating metal ion such as zinc. Further corrosion resistance is obtained by conventional means when the phosphatised surface is post-treated with a dilute aqueous acidic solution containing a chromium compound, usually a hexavalent chromium compound. Chromium and molybdate and complex oxide treatments are also employed.

Particular examples of processes for forming conversion coatings on metallic surfaces have been described in Metal Handbook, Volume II, 8th Edition, pages 529 to 547 of the American Society for Metals, and in Metal Finishing Guidebook and Directory, pages 590 to 603 (1972). Typically, the process calls for the following steps:

1. Cleaning;
 2. Water Rinsing;
 3. The formation of a conversion coating by contact with a suitable phosphate, chromate, or similar conventional bath;
 4. Water Rinsing;
 5. Post-treating with a dilute hexavalent chromium-containing composition;
- and

6. Optionally, drying the surface.

Zinc, iron and aluminium surfaces may all be conversion coated with suitable conversion-coating compositions. Examples of such metals include cold-rolled, ground, pickled and hot-rolled steel and galvanised steel.

The use of chromium-containing post-treatments, while satisfactory from a corrosion standpoint, has become environmentally objectionable.

In our Application No. 19007/73 (Serial No. 1,430,020) we have described and claimed a process which comprises coating a metallic surface with a conversion coating containing iron or zinc and phosphate ions and subsequently coating the thus-coated surface with a tannin-containing composition.

We have now found that superior results are obtained, comparable to those obtained when a conventional dilute hexavalent chromium-containing composition is employed, if the tannin-containing composition of our earlier invention also includes a melamine-formaldehyde resin. The results obtained by the process of the present invention are far superior to those using a tap or deionised water rinse when painted and tested for corrosion resistance.

Processes which comprise contacting a bare metal surface with tannin/melamine-formaldehyde containing compositions are described and claimed in our Application No. 42127/75 (Serial No. 1,520,027).

The exact composition of the melamine-formaldehyde resin suitable for use in the present invention does not appear to be critical. Monomeric, dimeric, and higher order resins have been found suitable. It is known that formaldehyde methylolates the amine groups of the melamine heterocycle after which cross-linking between the molecules takes place via condensation polymerisation. The degree of methylation is not critical although preferably there is at least one mole of formaldehyde per mole of melamine and more preferably at least 1.5 moles of formaldehyde per mole of melamine. The commercially available melamine-formaldehyde resins may also include various degrees of alkyl substitution with, for example, methyl, ethyl, propyl or butyl groups. Table I lists a number of the commercially available melamine-formaldehyde resins and their suppliers.

The range of concentration and pH values for suitable post-treatment results are selected depending upon the particular organic components employed. Improvements in the corrosion resistance as measured by the salt spray tests can be obtained at resin concentrations as low as 0.01 g/l. Increased concentrations produce further improvements in the corrosion resistance but excess resin concentrations, e.g. above 100 g/l, tend to cause the degradation in the corrosion resistance as measured by the humidity test. Preferably the resin concentration should be maintained at a value of from 0.25 to 25 g/l, to obtain best overall corrosion characteristics.

The use of tannins for the treatment of metal surfaces in general has been described in U.S. Patent Specifications Nos. 566,037; 750,986; 1,079,453; 1,501,425; 1,798,218; 1,817,174; 2,311,563; 2,854,368; 3,547,710; and 3,578,508; in U.S. Reissue Specification No. 24,604 and in our British Application No. 42313/74 (Serial No. 1,476,240). It is desirable to include at least 0.01 g/l of the vegetable tannin in the solution. Preferably, at least one part by weight of resin is used per part by weight of tannin. More preferably, the weight ratio of the resin to the tannin is at least 3.75:1 and most preferably at least 7.5:1. Table II lists names of various tannins which may be employed in the present invention together with their suppliers.

TABLE I.

MELAMINE-FORMALDEHYDE
RESINS

Code	Name	Supplier
R1	CR2024	Clark Chemical Corp.
R2	Resin G—3	Jersey State Chemical Co.
R3	Mel-Iron A	Crown Metro Inc.
R4	Schercomel Resin M	Scher Bros. Inc.
R5	X—3387	Cargill, Inc.
R6	Uformite MM—83	Rohm & Haas Co.
R7	Resydrol WM 501	American Hoeschst Corp.
R8	Resimene X 712	Monsanto Co.

TABLE I (continued).

MELAMINE-FORMALDEHYDE
RESINS

Code	Name	Supplier
R9	Resimene X 714	Monsanto Co.
R10	Resimene X 720	Monsanto Co.
R11	Resimene X 730	Monsanto Co.
R12	Resimene X 735	Monsanto Co.
R13	Resimene X 740	Monsanto Co.
R14	Cymel 370	American Cyanamid Co.
R15	Aerotex MW	American Cyanamid Co.
R16	Aerotex 92	American Cyanamid Co.
R17	Tanak M3	American Cyanamid Co.
R18	Aerotex P225	American Cyanamid Co.
R19	Tanak MRX	American Cyanamid Co.
R20	Cymel 7273—7	American Cyanamid Co.

TABLE II.

TANNINS

Code	Name	Supplier
T1	Tannic Acid	Merck & Co., Inc.
T2	Tannic Acid (NPF11)	S. B. Penick & Co.
T3	Tannic Acid (Tech. 3C)	The Harshaw Chemical Co.
T4	Tannic Acid (Tech. XXX)	"
T5	Tannic Acid (Tech 7c)	"
T6	Chestnut Extract	The Mead Corp.
T7	Spray Dried Chestnut	Arthur C. Trask Corp.
T8	Bisulfited Quebracho Extract	"
T9	Non-bisulfited Quebracho Extract	"
T10	Wattle Extract	"
T11	Cutch Extract	"

The pH to which the post-treatment solution should be adjusted may be readily determined for a particular resin-tannin combination by simple experiments at different pH levels and values as low as pH 2 and as high as pH 10 have been found to yield suitable anti-corrosive properties with pH values of from 6 to 9 being preferred.

While the melamine-formaldehyde resin or tannin components may be separately supplied and dissolved in the aqueous working solution, they are more conveniently supplied as a concentrate composition containing an aqueous solution of from 1 to 80 weight % of the melamine-formaldehyde resin and 1 to 40 weight % of the vegetable tannin, the percentages being based on the total weight of the concentrate. This concentrate, which forms a second aspect of the present invention, may then be diluted to the desired concentration for use.

The method of drying the workpiece following the post-treatment will depend upon the desired anti-corrosive properties. While room-temperature drying may be employed, it is preferred to employ dry-off temperatures in excess of about 250°F.

Any conventional method of application such as spray-on, immersion, and roll-on are suitable.

Although the post-treatment solution may be heated, improved results are obtained operating at room temperatures or slightly above, e.g. 100°F. The period of contact between the metal surface and the post-treatment solution is not critical, and periods of a half a minute give excellent results.

In the Examples which follow and which illustrate the invention, the phosphate-containing compositions give a conversion coating, on the metal surface, which contained iron or zinc and phosphate ions. The following test procedures, definitions and, in Table III, types of paint were used.

SALT SPRAY CORROSION RESISTANCE.

Salt spray corrosion resistance was measured in accordance with the procedure of ASTM B117—61. The panels were rated in terms of the amount of paint loss from a scribe in 1/16 inch increments (N for no loss of paint in any point). The principal numbers represent the general range of the creepage from the scribe along its length whereas the superscripts represent spot or non-representative creepage at the point of maximum creepage along the length of the scribe. Thus, 2—7^{10s} means representative creepage varied from 2/16 to 7/16" with a maximum of 10/16" at one or two spots. Where corrosion was extensive, the results were expressed as percent peel over the entire panel surface, e.g. 60%P.

HUMIDITY CORROSION RESISTANCE.

Humidity corrosion resistance was measured in accordance with the procedure of ASTM 2247—64T. The panels were rated in terms of the number and size of the blisters: F for few, M for medium and D for dense, and from 9 for very small size to 1 for very large. 10 represents no blisters. Where the rating is preceded by a G or C, the panel gave a 10 rating except for blisters due to handling (G) or concentration effects (C) such as those which would result from solution run down.

TOTAL ACID.

Milliliters of 0.1 N NaOH added to a 10 ml. sample to the phenolphthalein end point.

FREE ACID.

Milliliters of 0.1 N NaOH added to a 10 ml. sample to the methyl orange or bromo-cresol green endpoint.

TABLE III.

Name	Paints	Description	Manufactured by
Dulux 704—6731		White alkyd	DuPont Company
DuPont 963—72724		White acrylic	"
PPG 222—1005		Black Modified alkyd primer	PPG Industries, Inc.
Duracron 200		Acrylic	"

In the examples, all concentrations are net solids unless otherwise specified.

EXAMPLE 1.

An aqueous alkali metal phosphate solution was prepared in a five gallon laboratory spray tank from sodium dihydrogen phosphate and sodium chlorate. The phosphate solution, which contained 10 g/l phosphate ions and 5 g/l chlorate ions, was heated to 160°F. A number of 4" x 12" CRS panels were given a conventional spray clean for one minute at 160°F, and were then hot water rinsed for 1/4 minute, spray coated in the alkali metal phosphate solution for one minute, cold water rinsed for 1/4 minute, and spray rinsed for 1/4 minute in a solution containing 3 g/l of resin R19 and 0.19 g/l of resin T9. The solution was adjusted to pH 10.0 with 25% H₃PO₄ and oven dried for 5 minutes at 275°F. Control panels were prepared in a similar manner, except that they were oven dried following a one minute cold water rinse after the alkali metal solution treatment step, or alternatively treated in a commercial post-treatment containing 0.1% chromic acid at a pH of about 2.5 at 80°F and oven dried.

The panels were finished with the Dulux 704—6731 paint and subjected to the standard salt spray test for 168 hours and the standard humidity test for 336 hours. The results are presented in Table IV.

TABLE IV.

Post-Rinse	Salt Spray (168 Hr.)
Resin/Tannin	0—1 ^{2s}
Chromium	0—1
Tap Water	7—8 ^{10s}

These results show that the process of the invention is superior to processes using tap water as a final rinse, and nearly as good as commercial processes using chromium-containing rinses under salt spray conditions. All humidity results were excellent, giving ratings of 10.

COMPARATIVE EXAMPLE A.

The procedure of Example 1 was repeated except that a number of different post-treatment solutions were prepared containing varying quantities of resin R19 and having pH values ranging from 8 to 10. Controls using tap water, deionised water, and chromium rinses were run as before. The results are tabulated in Table V. While the resin solution imparted a corrosion-resistance better than that obtained with tap water or deionised water, the corrosion resistance did not compare with that obtained with the conventional chromium process.

TABLE V.

Resin R19 without Tannin Resin Conc. — g/l	Salt Spray (168 Hrs.) at Solution pH		
	pH8	pH9	pH10
0.5	7—8 ^{9s}		
"		8—9	
"			7—8
1.0	5—6 ^{7s}		
"		8—9	
"			6—7 ^{8s}
2.0	3—5		
"		3—7	
"			3—7
4.0	2—4		
"		2—4	
"			2—4
Controls			
Tap Water	6—8		
Deionised Water	7—8		
Chromium	0—1 ^a		

COMPARATIVE EXAMPLE B.

The procedure of Example 1 was again repeated except that a solution containing only tannin T9 at varying concentrations and varying pH's was employed as the post-treatment. The results set out in Table VI show that the corrosion resistance obtained with the solution containing the tannin alone does not compare with the conventional chromium rinse, in the same way as the solution containing the melamine-formaldehyde resin alone does not (see Comparative Example A).

TABLE VI.

Tannin T9 without Resin Tannin Conc. — g/l	pH	Salt Spray (168 Hr.)
0.125	7.7	5—7
"	8.0	3—4 ^{5s}
"	10.0	4—5
0.25	7.7	6—6
"	9.0	4—5
"	10.0	4—4

TABLE VI (continued).

Tannin T9 without Resin Tannin Conc. — g/l	pH	Salt Spray (168 Hr.)	
0.50	7.9	6—7	
"	9.0	4—5	
"	10.0		6—7 ^{8a}
1.0	7.9	6—8	
"	9.0	5—6 ^{7a}	
"	10.0		6—7
2.0	8.0	6—8	
"	9.0	7—8 ^{9a}	
"	10.0		7—8 ^{9a}
Controls			
Tap Water	5—7		
Deionised Water	6—7 ^{8a}		
Chromium	N		

EXAMPLE 2.

The procedure of Example 1 was repeated except that separate post-treatment solutions were prepared to contain 4 g/l of different melamine-formaldehyde resins with the pH adjusted to 9.0, and both with and without 0.25 g/l of tannin T9. The salt spray results after 168 hours are reported in Table VII. Controls were run as in the previous examples. The results show that the combination of the resin and the tannin gave far superior corrosion resistance, as measured by the salt spray test, as compared with the use of resins alone.

TABLE VII.

Melamine-Formaldehyde Resin	Salt Spray (168 Hrs.)	
	Without Tannin	With Tannin T9
R1	4—6 ^{8a}	0—1
R2	2—6 ^{8a}	0—1
R3	4—7 ^{8a}	0—1
R4	2—4 ^{6a}	0—1
R5	3—6	0—1 ^a
R6	2—5	0—1 ^a
R7	4—8 ^{9a}	0—1
R8	4—8	0—1
R9	2—7 ^{10a}	N

TABLE VII (continued).

Melamine-Formaldehyde Resin	Salt Spray (168 Hrs.)	
	Without Tannin	With Tannin T9
R10	5—8 ^{9s}	0—1
R11	4—7	0—1 ^{2s}
R12	6—9 ^{10s}	0—1
R13	3—5 ^{6s}	0—1
R14	5—8 ^{9s}	0—1
R15	4—9	0—1
R16	2—5 ^{6s}	0—1
R17	5—7	4—6
R18	6—8	1—2
Controls		
Tap Water	6—8 ^{9s}	
Deionised Water	5—8 ^{10s}	
Chromium	0—1	

EXAMPLE 3.

The procedure of Example 1 was again repeated except that separate post-treatment solutions were prepared to contain 4 g/l of resin R19 and 9.25 g/l of various types of tannins, the solutions being adjusted to pH values ranging from 4 to 8. When the salt spray results, after 336 hours, are compared with those of the controls in Table VIII, it is observed that the post-treatment solution containing both the resin and the tannin produces a much greater degree of corrosion resistance over a broad range of pH values than that obtained through the use of tap water, deionised water, or either the resin or tannin alone. Results obtained are as good or almost as good as those obtained with the use of the dilute chromium-containing rinse.

TABLE VIII.

Resin R19 plus Tannin	Salt Spray (336 Hr.) at Solution pH		
	8.0	6.0	4.0
T1	1—1 ^{2s}	1—1 ^{4s}	1—3 ^{4s}
T2	0—1 ^s	0—1	1—1
T3	0—1 ^{2s}	0—1 ^{2s}	1—1 ^{2s}
T4	0—1	0—1 ^{3s}	1—2 ^{5s}
T5	1—3	1—2 ^{7s}	2—4 ^{8s}
T6	1—3	1—3 ^{4s}	1—3 ^{4s}

TABLE VIII (continued).

Resin R19 plus Tannin	Salt Spray (336 Hr.) at Solution pH		
	8.0	6.0	4.0
T7	1—1 ^{2a}	1—1 ^{2a}	1—4
T8	0—1	1—2	1—2
T9	0—1 ^a	0—1 ^a	0—1 ^a
T10	0—1	0—1	0—1 ^{2a}
T11	0—1	0—1	0—1 ^a

Controls

	Tap Water	45%P	
5	Deionised Water	55%P	5
	Chromium	0—1	
	Resin R19 only, pH 7	4—12 ^{15a}	
10	Tannin T9 only, pH 5	8—11 ^{15a}	10

EXAMPLE 4.

The procedure of Example 1 was repeated except that the post-treatment solution was made up to contain 4 g/l of resin R19 plus tannin T9. The pH was adjusted to 8.5 and the weight ratio between the resin and the tannin in the solution was varied while maintaining the total concentration of 4 g/l. Panels were separately tested with Dulux 704—6731 and the Duracron 200 paint. The salt-spray results after 168 hours are given in Table IX. These results show that a weight ratio of resin to tannin of at least 1:1 is preferable, in order to obtain salt spray results approaching those obtained with the conventional dilute chromium rinse. A ratio of 3.75:1 or above produces results as good as or better than those obtained with a dilute chromium rinse. While the paint employed affects the overall salt spray results, the post-treatment improves the corrosion resistance for both paint systems.

TABLE IX.

Wt. Ratio Resin/Tannin	Salt Spray (168 Hrs.) Dulux 704—6731 Paint	Salt Spray (168 Hrs.) Duracron 200 Paint
1/30	7—9	70% P
1/15	4—7	60% P
1/7.5	4—5	5—8
1/3.75	5—8	85% P
1/1	1—4	3—3 ^{4a}
3.75/1	0—1 ^a	0—1

TABLE IX (continued).

Wt. Ratio Resin/Tannin	Salt Spray (168 Hrs.) Dulux 704—6731 Paint	Salt Spray (168 Hrs.) Duracron 200 Paint
7.5/1	N	0—1 ^a
15/1	N	0—1
30/1	0—1	0—1 ^{2s}

Controls

	Tap Water	9—10	3—4	
5	Deionised Water	8—10	2—3	5
	Chromium	0—1 ^a	0—1	

EXAMPLE 5.

10 The procedure of Example 4 was repeated except that the weight ratio of the resin to the tannin was maintained at 16:1 while the resin concentration was varied from 0.2 to 6.4 g/l. The pH was maintained at a value of 7.0. The results are shown in Table X. These results show that at the weight ratio employed, a resin concentration of above 0.4 g/l is necessary in order to obtain salt spray corrosion results approaching those obtained with the dilute chromium rinse. As the concentration of resin increased to the level of 6.4 g/l, the humidity resistance decreased to 9.

EXAMPLE 6.

20 The procedure of Example 5 was repeated except that resin R20 was employed in place of resin R19 and the weight ratio of the resin to the tannin was adjusted to 7.5:1. The results are given in Table XI. These results show that, at the weight ratio and pH values employed, a resin concentration in excess of 0.45 g/l is desirable in order to obtain salt spray results comparable to those obtained with the dilute chromium rinse.

TABLE X.

Resin R19 Concentration-g/l	Salt Spray (336 Hr.)
0.2	60% P
0.4	2—5
0.8	1—1
1.6	0—1
3.2	0—1
6.4	0—1

Controls

25	Tap Water	80% P	25
	Deionised Water	90% P	
	Chromium	0—1	

TABLE XI.

Resin R20 Concentration-g/l	pH	Salt Spray (168 Hr.)
0.45	9.2	3—5
0.90	9.7	1—1
1.35	9.9	0—1*
1.8	9.9	1—2
1.8	4.0	1—2

Controls

Tap Water	7—10
Deionised Water	9—10
Chromium	0—1*

EXAMPLE 7.

An aqueous alkali metal phosphate coating solution was prepared in a five gallon laboratory spray tank from sodium dihydrogen phosphate and sodium chlorate. The phosphate solution, which contained 10 g/l phosphate ions and 5 g/l chlorate ions, was heated to 160°F. In a second spray tank, a conventional alkaline cleaner was prepared at a concentration of one ounce per gallon and was heated to 150°F. In a third spray tank, a post-rinse solution containing a water soluble melamine-formaldehyde resin and a condensed tannin was prepared by dissolving 80 grams Resin R19 and 20 grams of a solution consisting of 25 parts tannin T9, 1 part NaOH, and 74 parts water in twenty litres water. The solution (which contained 4 g/l Resin and 0.25 g/l Tannin) had a pH, as prepared, of approximately 8 but was adjusted, before use, to a value of 6.4 with 25% phosphoric acid. All post-treatment rinses were used at ambient temperatures. A number of 4" x 12" SAE 1010, cold rolled, steel panels were sprayed in the following sequence: one minute cleaner, ½ minute fresh warm water rinse in an auxiliary spray tank; one minute alkali metal phosphate coating solution; ½ minute cold water rinse; and ½ minute resin/tannin post-treatment solution; after which they were dried in a circulating air oven for five minutes at 325°F. Other sets of panels were processed similarly, except that the pH of the post-rinse solution was adjusted to values of 5.2 and 3.0 with 25% phosphoric acid. Control panels were prepared in the same manner except that they were oven dried following the cold water rinse, or alternatively treated in a commercial post-treatment solution containing approximately 0.1% chromic acid for ½ minute following the cold water rinse and oven dried.

The panels were divided into three sets and then finished with three different paint systems. After finishing, the panels were subjected to the standard salt spray test for 336 hours, the results of which are shown in Table XII.

TABLE XII.

Post-Treatment pH	Dulux 704—6731	DuPont 963—72724	PPG 222—1005
6.4	0—1*	0—1*	0—1 ^{4s}
5.2	0—1	N	1—1 ^{3s}
3.0	2—5 ^{6s}	0—1*	1—1 ^{2s}

Controls

Chromium	0—1	0—1 ^a	0—1
Tap Water	80%P	9—12	2—4

5 The results show that, under the conditions employed with the melamine-formaldehyde resin/tannin rinse, corrosion resistance as measured by salt spray is much better than with a tap water rinse and nearly as good as that given by a conventional chromium containing rinse over a wide range of pH values regardless of the type of paint employed. More consistent results are obtained above pH 3.

EXAMPLE 8.

10 Aluminium, zinc galvanized and cold-rolled steel panels were treated with various phosphatizing solutions and post-treated with a melamine-formaldehyde resin and tannin solution with a weight ratio of resin to tannin of approximately 16:1. The phosphate baths employed included various combinations of chlorate, fluoride, nitrate, nickel, zinc, molybdate, and ammonium ions. As in the previous
15 examples, the post-treatment of the present invention was employed at a concentration of about 4 g/l. The salt spray corrosion resistance was better than that obtained with tap water or deionised water and, in most cases, comparable to that obtained with the use of the conventional dilute chromium rinse.

EXAMPLE 9.

20 The procedure of Example 1 was repeated except that the post-treatment solution contained 1.6 g/l of resin R9 and 0.22 g/l of tannin T9, adjusted to a pH of 8.0. The bath was maintained at room temperature while the temperature of oven drying was varied from 275 to 425°F. Results are shown in Table XIII. These
25 results show that while improved corrosion resistance can be obtained at low dry-off temperatures, elevated temperatures are preferred in order to obtain corrosion resistance comparable to that obtained for the dilute chromium rinse.

EXAMPLE 10.

30 The procedure of Example 1 was repeated except that the post-treatment solution contained 1.6 g/l of resin R20 and 0.22 g/l of tannin T9, adjusted to a pH of 8.5—8.8. The bath was maintained at room temperature while the temperature of oven drying was varied from 250 to 450°F. The time in the oven was varied from 1 to 5 minutes. Salt spray results after 336 hours are shown in Table XIV. These
35 results show that while much improved corrosion resistance can be obtained by air drying or short time-low temperature dry-offs, longer time-higher temperature dry-offs are preferred in order to obtain corrosion resistance comparable to that obtained for a dilute chromium rinse.

TABLE XIII.

Oven Temperature — °F	Salt Spray (336 Hr.)
275	3—3 ^{8s}
325	0—1 ^{3s}
350	0—1 ^{7s}
375	1—3 ^{5s}
425	1—2 ^{4s}

Controls

Deionised Water	96% P
Chromium	0—1

TABLE XIV.

Time — Min.	Oven Temperatures — °F	Salt Spray (168 Hr.)
—	Air Dried	2—3
5	250	1—1
5	300	0—1
1	350	1—2
3	350	0—1
5	350	0—1
5	400	0—1
5	450	0—1

Controls

Chromium

0—1

Deionised
Water

50%P

EXAMPLE 11.

An aqueous acidic zinc phosphate coating solution was prepared in a five gallon laboratory spray tank to contain 1.2 g/l zinc ions, 1.0 g/l nickel ions, 1.0 g/l fluoride (added as silicofluoride), 5.0 g/l phosphate ions, 2.0 g/l nitrate ions and 0.1 nitrite ions. This solution, when heated to 150°F, was found to have a total acid of between 13.0 and 14.6 points, and a free acid of between 1.0 and 1.3 points. In a second spray tank, a conventional alkaline cleaner was prepared at a concentration of one ounce per gallon and was heated to 145 to 150°F. A third spray tank was used to contain the melamine-formaldehyde resin/tannin post-treatment solutions detailed in Table XV.

A number of 4" x 12" SAE 1010, cold rolled steel panels (CRS) and 4" x 12" minimum spangle commercial hot-dipped galvanized panels (GALV), temper rolled one percent, were sprayed in the following sequence: one minute cleaner; $\frac{1}{4}$ minute fresh warm water spray rinse; one minute zinc phosphate solution; $\frac{1}{4}$ minute cold water rinse; and $\frac{1}{4}$ minute melamine-formaldehyde resin/tannin solution as detailed in the Table, after which they were dried in a circulating air oven for five minutes at 325°F. Control panels were prepared in the same manner except that they were oven dried following a $\frac{1}{4}$ minute tap water rinse and a $\frac{1}{4}$ minute deionised water rinse or alternatively treated in a commercial post-treatment solution, containing about 0.04% chromic acid, at a pH of about 4 at 80°F for $\frac{1}{4}$ minute following the cold water rinse, and oven dried. Other control panels were prepared in the same manner except that they were treated in a solution containing 0.25 g/l of tannin T9 at a pH of 4.6 (adjusted with H_3PO_4) at 80°F for one-half minute following the cold water rinse and oven dried. In this example, all panels were oven dried for 5 minutes at 325°F.

The treated panels were finished with Dulux 704—6731 or a three coat automotive body paint system consisting of an epoxy primer, an epoxy guide coat and a thermoset acrylic topcoat, and then subjected to salt spray and humidity testing for 336 hours. System A contains 0.8 g/l R9 and 0.11 g/l T9, adjusted to pH 8.6 with NaOH. System B contains the same concentrations of components, adjusted to pH 9.0. System C contains 0.85 g/l R19 and 0.056 g/l T9, adjusted to pH 9.0 with NaOH. The results are given in Table XV. The results show the corrosion resistance imparted employing the resin/tannin post-treatment over a zinc phosphate coating are comparable to that obtained with a conventional chromium rinse and much better than that obtained using deionised water or the tannin alone.

TABLE XV.

Post-Treatment	Metal	Automotive Body System		Dulux 704—6731	
		Salt Spray (336 Hr.)	Humidity (336 Hr.)	Salt Spray (336 Hr.)	Humidity (336 Hr.)
A	CRS GALV	0—1 N	10 ¹ 10	2—3 0—1	VF9 10
B	CRS GALV	0—1 ^s N	10 10	3—5 0—1	10 10
C	CRS GALV	0—1 ^s N	10 C9	1—2 1—1	10 10
<u>Controls</u>					
Chromium	CRS GALV	0—1 ^{3s} N	10 10	3—6 0—1 ^s	VF9 10
Deionised Water	CRS GALV	3—4 2—3	10 C9	10—12 ^{14s} 4—6 ^{7s}	C8/F9 10
Tannin T9 0.25 g/l pH 4.6	CRS GALV	0—2 N	10 10	3—7 1—1 ^{2s}	VF9 10

WHAT WE CLAIM IS:—

1. A process of treating a metal surface comprising coating the surface with a conversion coating containing iron or zinc and phosphate ions and subsequently coating the thus-coated surface with an aqueous solution containing a melamine-formaldehyde resin and a vegetable tannin.
2. A process according to claim 1 in which the solution contains at least 0.01 g/l of the resin.
3. A process according to claim 1 or claim 2 in which the solution contains not more than 100 g/l of the resin.
4. A process according to claim 1 in which the solution contains from 0.25 to 25 g/l of the resin.
5. A process according to any preceding claim in which the solution has a pH of not more than 10.
6. A process according to claim 5 in which the solution has a pH of from 6 to 9.
7. A process according to any preceding claim in which the treated surface is dried at an elevated temperature.
8. A process according to any preceding claim in which the solution contains at least 0.01 g/l of the tannin.
9. A process according to any preceding claim in which the solution contains at least one part by weight of resin per part by weight of tannin.
10. A process according to claim 9 in which the solution contains at least 3.75 parts by weight of resin per part by weight of tannin.
11. A process according to any preceding claim in which the solution is substantially free of chromium.
12. A process according to claim 1 substantially as herein described with reference to the Examples.
13. A metal surface when treated by a process according to any preceding claim.
14. An aqueous working solution suitable for use in the process of claim 1 and comprising at least 0.01 g/l of a melamine-formaldehyde and resin and at least 0.01 g/l of a vegetable tannin.
15. An aqueous concentrate which comprises from 1 to 80% by weight of a

melamine-formaldehyde resin and from 1 to 40% by weight of a vegetable tannin, the percentages being based on the total weight of the concentrate.

16. A solution according to claim 14 or a concentrate according to claim 15 which contains at least one part by weight of resin per part by weight of tannin.

17. A solution or concentrate according to claim 16 which contains at least 3.75 parts by weight of resin per part by weight of tannin.

18. A solution or concentrate according to any of claims 14 to 17 which is substantially free of chromium.

19. A solution according to claim 14 or a concentrate according to claim 15 substantially as herein described with reference to the Examples.

For the Applicants,
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
53/64 Chancery Lane,
London, WC2A 1HN.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

THIS PAGE BLANK (USPTO)